

DETECTION AND DECONTAMINATION KINETICS OF VX AND RELATED COMPOUNDS BY LC/MS

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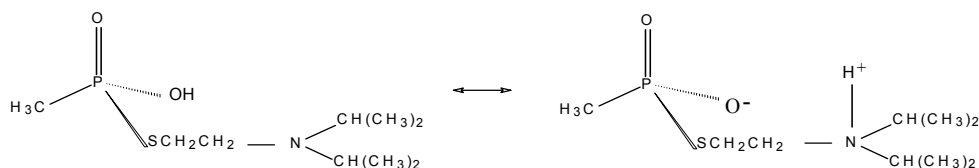
ABSTRACT

Liquid Chromatography/Mass Spectrometry (LC/MS) and Nuclear Magnetic Resonance Spectrometry (NMR) analytical methods were tested for the detection of EA-2192 in caustic monoethanolamine (MEA) decontamination solution. Precision and accuracy testing was done for the LC/MS method which gave a minimum detection limit (MDL) of 7.6 ng/mL after dilution, or 760 ng/mL in the original solution, which was adequate for the study and gave better sensitivity than NMR. The spike recovery was 70%. The method was used to measure the kinetics of VX and EA-2192 reaction at temperatures of 25 and 50 C. Half life of VX in the solution at 50 C was 5 min. or less, but the half life of EA-2192 was 56 min. For runs at room temperature, the decrease in the EA-2192 concentration was much slower. Results from NMR analyses were in good agreement.

INTRODUCTION

Some decontamination methods that are being studied to destroy chemical weapons involve liquid phase reactions to chemically degrade the agents into other products. Liquid decontamination solutions present analytical problems, since the complex mixtures must be analyzed. Analytical screening sensitivity that is required for the primary stage of decontamination is usually dictated by US EPA, Army, and state regulations.

One of the important chemical weapons agents is VX. This compound is a phosphonothiolate with tertiary amine group. It has low volatility at room temperature, but can be analyzed by GC techniques, as well as LC/MS and NMR. A decontamination product of VX is called EA-2192 [S,2-(diisopropylaminoethyl) methylphosphonothioic acid].



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This compound is both a phosphonic acid and amine that forms nonvolatile zwitterion in neutral aqueous solution. There have been studies to analyze this compound by chemically derivatizing and analyzing by GC, with some success.¹⁻³ However, the simplest analytical methods for detecting EA-2192 in decontamination solution are by LC/MS or ³¹P NMR.

Caustic monoethanolamine decontamination solution (81% MEA, 5% NaOH) was one type of matrix that has been studied to decontaminate VX. This matrix was chosen in order to minimize the formation of EA-2192, which commonly forms in aqueous caustic decontamination. It was found that little EA-2192 is formed in this decontamination solution.^{3,4} The present study is concerned with measuring the kinetics of the destruction of the small amount of EA-2192 that was formed.

EXPERIMENTAL METHODS

The most promising trace-level method for detection of VX and EA-2192 in the decontamination solution is LC/MS. The detection limits in decontaminant are not as good as environmental samples. Problems are caused by the high concentration of decontamination reagents and products. Dilution of samples by 1:100 is necessary to be compatible with LC mobile phase to obtain good performance of the method in the presence of potential interferences.

The parameters of the LC/MS Method are as follows:

Instrument: Agilent LC/MSD with 1100 LC and autosampler

LC column: Phenomenex Luna or Polar-RP column, 150 mm long by 2.0

mm i.d. column, and 4.0 μ m particle size. (reversed phase chromatography column)

Flow rate: 0.25 mL/min.

Mobile phase: Gradient

0-10 min.: 97.5% DI water, 2.5% acetonitrile, 1% acetic acid

20 min.: 50% DI water, 50% acetonitrile, 0.5% acetic acid

40 min.: return to 97.5% water to equilibrate column

Flow splitting: 1:5 liquid flow to waste

MSD ion source: Electrospray

Capillary voltage: 4000 V

Dry Gas flow: 9 L/min.

Nozzle gas press.: 50 psig

Gas Temp: 300°C

Other MSD conditions: According to Autotune using ESI tune solution

Injection volume: 25 μ L

Detection method: SIM or Scan

SIM Detection ions: 240 (fragmenter = 120V)

The sample preparation involves dilution of decontamination solution by a factor of 1:100 by volume in a solution of 10% acetic acid in water. This preparation quenches the decontamination reaction.

A Minimum Detection Limit (MDL) test of the LC/MS method was done for EA-2192 using a two-day MDL study.³ The MDL that is determined from the study is 7.6 ng/mL, uncorrected for dilution. The percent recovery was 79%. Corrected for dilution of the samples by 1:100 during the sample preparation, the MDL results are 0.76 μ g/mL in the original decontamination solution. The concentration of VX was analyzed for these runs using the same LC/MS procedure. The sensitivity for VX was similar to that of EA-2192, but the MDL was not determined.

Another important method for detecting EA-2192 is phosphorus-31 NMR. ^{31}P NMR has been an important method for nerve agents. Sensitivity can be as low as $10\text{ }\mu\text{g/mL}$ for a 300 MHz instrument, depending on interferences and run times. The EA-2192 chemical shift is strongly pH dependent, and interferences are present in the decon solution. Some kinetic determinations were done using NMR by periodically remeasuring spectra of the same sample over a period of time to confirm the LC/MS results.

Kinetic determinations of the rate of decontamination of EA-2192 in caustic monoethanolamine decontamination solutions were studied. The decontamination solution was spiked with either neat VX or a 10% solution of EA-2192 in isopropanol to a specified concentration. Aliquots of the solution were withdrawn using a pipet at measured time intervals, diluted by 1:100 to quench the reaction, and analyzed by the LC/MS method.

RESULTS

Figure 1 shows the data for the concentration of EA-2192 as a function of reaction time for four reaction runs that begin with 5% VX in caustic monoethanolamine solution and which were run at 50-55°C. The log of EA-2192 concentration is plotted as a function of time. The trend line that is shown in the figure is for the 3/27 run #1. (On the log scale, 50 ppm = 1.699, which was the target concentration for the project.)

Other kinetic determinations included the study of VX in the same 5% VX decontamination solution. The VX was destroyed to >99% in less than 15 min. However, a background signal of a residual amount of VX could be detected for considerably longer than 15 min. for the 50-55°C runs. The VX signal does not appear to be an interference, in that it meets the detection criteria for VX in terms of LC retention time and mass spectrometer ion signals. It also does not decrease in a smooth, reproducible, exponential fashion that would be expected of a kinetic reaction. The amount was too small to be detected by NMR for confirmation. Figure 2 shows the log of the VX concentration as a function of time, starting with 5% by volume of VX in the caustic monoethanolamine decontamination solution. By 200 min., the concentration was $<1\text{ }\mu\text{g/mL}$.

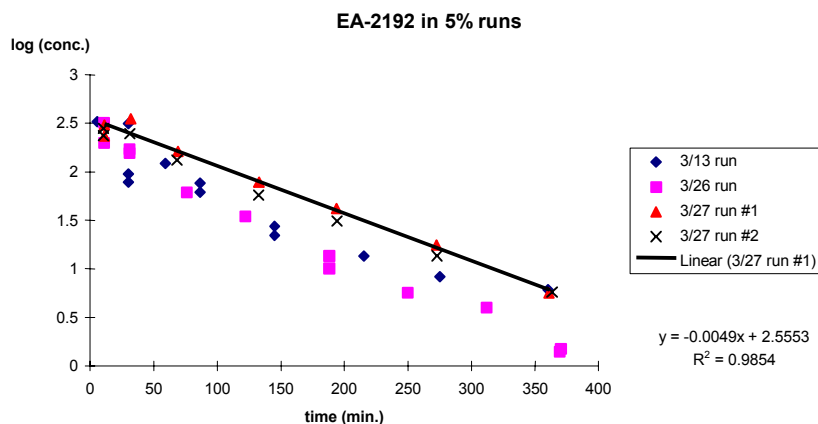


Figure 1. Data for the concentration of EA-2192 as a function of reaction time for four reaction runs that begin with 5% VX in caustic monoethanolamine solution and which were run at 50-55°C.

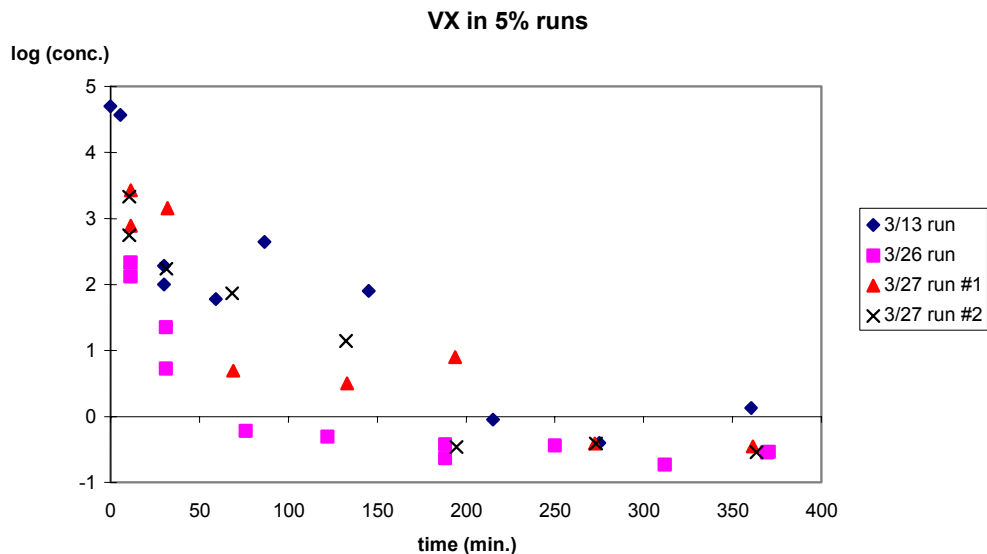


Figure 2. Log of the concentration of VX as a function of reaction time for four reaction runs that begin with 5% VX in caustic monoethanolamine solution and which were run at 50-55°C. A log value of 0 indicates a concentration of 1 $\mu\text{g/mL}$.

It is not certain why this residual VX is observed. It is possible that this VX is an analytical artifact from acidifying the samples before analysis. It has been previously reported that acidification of caustic MEA samples produces a signal corresponding to VX.⁵ This artifact may be a result of the presence of a chemical stabilizer in the VX. It was not observed in preliminary runs with a different VX standard.

Determinations were also done for reactions beginning with 1000 and 2000 ppm EA-2192 using the same decontamination solution composition at 50 C. Rates were consistent with the data in Figure 1. No VX was detected when EA-2192 was used as a reagent rather than VX.

A study of the rates for EA-2192 at room temperature was done. Results were obtained by detecting EA-2192 with both LC/MS and NMR, and the results were comparable for both techniques. Runs at room temperature were done to determine the stability of EA-2192 in the solutions in ambient storage conditions. At room temperature (about 20-25°C) the decrease was slow. The time required to decrease below 50 ppm was 300-400 hours, or 12-16 days. A similar study was done using detection by NMR of the EA-2192 peak. A sample of decontamination solution was spiked to about 125 $\mu\text{g/mL}$ and followed for two months. Results are shown in Figure 3. The EA-2192 reacted slowly over a period of weeks.

Although EA-2192 reacts slowly in caustic decon solutions, it reacts quickly in oxidizing solutions.⁶ Low concentrations of EA-2192 were consumed in less than 15 min. in pH 4 and pH 10 water solution after addition of bleach (sodium hypochlorite solution) to a concentration of 0.5%.

CONCLUSION

An LC/MS method was developed for EA-2192 and VX. The MDL for EA-2192 was determined to be 7.6 ng/mL after dilution, or 760 ng/mL in the original decontamination solution. For the runs at 50°C, the VX and EA-2192 concentrations were below the target concentration of 50 ppm in 200 min. or less.

The EA-2192 reaction was much slower than the VX reaction rate, and it has a half-life of 50-70 min. at 50°C. For runs at room temperature, the EA-2192 reacted much slower.

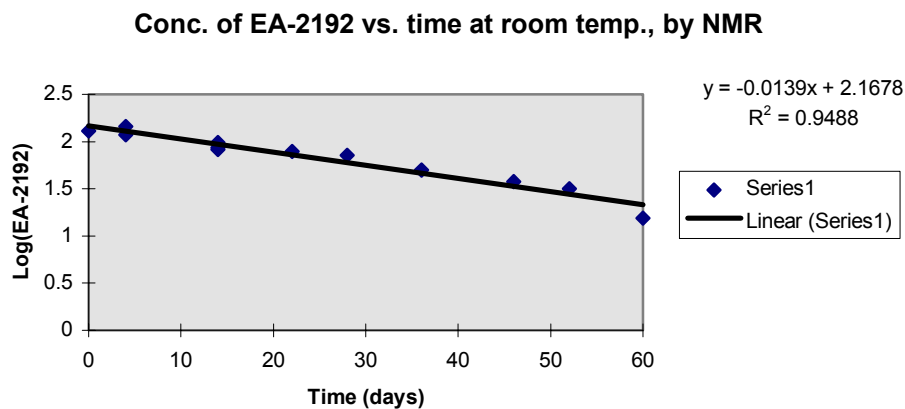


Figure 3. Log of the concentration of EA-2192 as a function of reaction time for a reaction run that began with 125 µg/mL EA-2192 in caustic monoethanolamine solution and was stored at room temperature(25 C).

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